

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 283 219 A2

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
12.02.2003 Bulletin 2003/07

(51) Int Cl.7: **C08C 1/04, C08J 3/22**
// C08L7:02

(21) Application number: **02255103.0**

(22) Date of filing: **22.07.2002**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **27.07.2001 JP 2001227748**
27.07.2001 JP 2001228123

(71) Applicant: **BRIDGESTONE CORPORATION**
Tokyo 104-0031 (JP)

(72) Inventors:
• **Yanagisawa, Kazuhiro,**
Bridgestone Cor. Tech. Cen.
Kodaira-shi, Tokyo 187-0031 (JP)
• **Someno, Kazuaki, Bridgestone Cor. Tech. Center**
Kodaira-shi, Tokyo (JP)
• **Mukai, Uchu, Bridgestone Cor. Tech. Center**
Kodaira-shi, Tokyo (JP)

(74) Representative: **Lamb, Martin John Carstairs**
MARKS & CLERK,
57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) **Natural rubber master batch, production method thereof, and natural rubber composition**

(57) The natural rubber master batch of the present invention is prepared by mixing a natural rubber latex having its amide linkages cleaved and an aqueous slurry having a filler dispersed in water. Alternatively, the natural rubber master batch is prepared by a method including a step for mixing a natural rubber latex and an aqueous slurry containing dispersed fillers having a spe-

cific particle size distribution and a limited range of 24M4DBP absorption. The natural rubber composition of the present invention is prepared by compounding natural rubber, which contains non-rubber components prepared by cleaving amide linkages of natural rubber latex, with silica and/or a particular inorganic filler.

EP 1 283 219 A2

Description**BACKGROUND OF THE INVENTION**

5 1. Field of the Invention

10 [0001] The present invention relates to a natural rubber master batch, a production method thereof, and a natural rubber composition. More specifically, the present invention relates to a natural rubber composition having improved in processability, reinforcing property and abrasion resistance, a natural rubber master batch suitable for producing the natural rubber composition, and a production method of the natural rubber maser batch.

2. Description of the Prior Art

15 [0002] Generally, natural rubber is known to be excellent in mechanical properties, low heat build-up, and abrasion resistance. In addition, natural rubbers receive attention as environmentally friend materials. Natural rubbers contain non-rubber components having amide linkages (protein). It has been known that the non-rubber component in natural rubber has an aging resistant effect and a vulcanization accelerating effect. In contrast, the non-rubber component has a drawback of reducing the processability of natural rubber as compared with synthetic rubbers because it increases the viscosity of rubbers by molecular chain entanglement caused by hydrogen bonding between amide linkages.

20 [0003] In recent special applications such as a natural rubber product for medical use, is used natural rubber having its non-rubber component such as proteins removed to a considerable extent by centrifugal separation of latex (Japanese Patent Application Laid-Open Nos. 6-56902, 8-143606, 11-71408, 2000-19801, etc.). Such natural rubber, however, involves a problem of a lowered elastic modulus and a poor aging property because the non-rubber component having the aging resistant effect and the vulcanization accelerating effect is removed nearly completely.

25 [0004] As a production method of rubbers of excellent processability, generally known is a method using a wet master batch. In this method, a slurry is prepared in advance by mixing a filler such as carbon black and silica with water in a certain proportion and then finely dispersing the filler throughout water by mechanical force. The slurry is then mixed with a rubber latex, followed by addition of a coagulant such as acids, inorganic salts and amines to coagulate the mixture, and recovery and drying of the coagulated product (Japanese Patent Publication Nos. 36-22729 and 30 51-43851).

[0005] As compared with a wet master batch for synthetic rubbers, a wet master batch comprising natural rubber and a filler such as carbon black, silica, other inorganic filler, etc. shows a smaller improving effect on the processability and has a drawback of hardly attaining a good dispersion of the filler. When excessively applying a mechanical shearing force to obtain a slurry with a good dispersion, aggregates (structures) of filler are broken to decrease the reinforcing 35 property and deteriorate the abrasion resistance.

SUMMARY OF THE INVENTION

40 [0006] An object of the present invention, in view of the foregoing, is to provide a natural rubber master batch for producing a natural rubber composition which is improved in the processability, the reinforcing property and the abrasion resistance.

[0007] Another object of the present invention is to provide a production method of the natural rubber master batch.

45 [0008] Still another object of the present invention is to provide a natural rubber composition having been greatly improved in the processability, and simultaneously, having been balanced in an anti skidding property on wet roads, a low fuel consumption and an abrasion resistance in high level, without adversely affecting the elastic modulus and aging characteristics attributable to natural rubber.

[0009] Further still another object of the present invention is to provide a tire which is produced by using the natural rubber composition.

50 [0010] As a result of intensive study in view of attaining the above objects, the inventors have found that the problems are solved by modifying known production methods of natural rubber master batches, and by using a natural rubber treated by a specific method so as to contain the non-rubber component. The present invention has been accomplished on the basis of this finding.

55 [0011] Thus, in a first aspect, the present invention provides a method for producing a natural rubber master batch, which comprises Step 1 for cleaving amide linkages in a natural rubber latex; and Step 2 for mixing the latex having its amide linkages cleaved with an aqueous slurry having been dispersed with at least one filler selected from the group consisting of carbon black, silica and an inorganic filler represented by the following Formula I:



wherein M^1 is at least one member selected from the group consisting of metals of aluminum, magnesium, titanium, calcium and zirconium, oxides of the preceding metals, hydroxides of the preceding metals, hydrates of the preceding oxides and hydroxides, and carbonates of the preceding metals; n is an integer of 1 to 5; x is an integer of 0 to 10; y is an integer of 2 to 5; and z is an integer of 0 to 10.

[0012] In a second aspect, the present invention provides a method for producing a natural rubber master batch, which comprises a step for mixing a natural rubber latex with an aqueous slurry having been dispersed with at least one filler selected from the group consisting of carbon black, silica and an inorganic filler represented by the above Formula I, wherein (i) the particle size distribution of the filler in the aqueous slurry is 25 μm or less in terms of a volume average particle size (mv) and 30 μm or less in terms of a 90 volume % particle size (D90), and (ii) a 24M4DBP absorption of dried filler recovered from the slurry is maintained at 93% or more of that of a filler before dispersed into water.

[0013] In a third aspect, the present invention provides a natural rubber master batch produced by mixing a natural rubber latex having amide linkages cleaved and a slurry having been dispersed with at least one filler selected from the group consisting of carbon black, silica and an inorganic filler represented by the above Formula I, and by coagulating the resultant mixture.

[0014] In a fourth aspect, the present invention provides a natural rubber composition comprising (A) a natural rubber containing non-rubber components obtained by cleaving amide linkages of a natural rubber latex, and (B) silica and/or an inorganic filler represented by the above Formula I.

[0015] In a fifth aspect, the present invention provides a tire produced by using the natural rubber composition.

DETAILED DESCRIPTION OF THE INVENTION

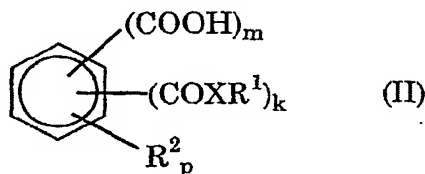
[0016] The first method of the present invention for producing the natural rubber master batch includes Step 1 for cleaving amide linkages in a natural rubber latex, and Step 2 for mixing the amide-linkage-cleaved latex with a slurry prepared in advance by dispersing into water at least one filler selected from the group consisting of carbon black, silica and the inorganic fillers of Formula I.

[0017] In Step 1, the cleavage of the amide linkages in the natural rubber latex can be carried out by various methods. Of the methods, a method using protease or a method using a derivative of aromatic polycarboxylic acid is preferably used.

[0018] In the method of using protease, the protease hydrolyzes amide linkages present in a surface layer of natural rubber latex particles. Examples of protease include acidic protease, neutral protease and alkaline protease, with the alkaline protease being preferred in the present invention in view of effectiveness.

[0019] The cleavage of the amide linkages by protease can be carried out under conditions optimum to enzyme to be mixed. For example, when a natural rubber latex is mixed with Alkalase 2.5L type DX manufactured by Novozymes A/S, the treatment is preferably conducted at 20 to 80°C. The pH range is usually 6.0 to 12.0. The amount of added protease is usually 0.01 to 2% by weight, preferably 0.02 to 1% by weight based on the natural rubber latex.

[0020] The derivative of aromatic polycarboxylic acid to be used in another method is represented by the following Formula II:



wherein:

m and k are each integer of 1 to 3, p is an integer of 1 to 4 while $m + k + p = 6$, when $m \geq 2$, the carboxylic groups, partly or entirely, may be form an acid anhydride group,

X is oxygen atom, NR^3 wherein R^3 is hydrogen atom or alkyl group having 1 to 24 carbon atoms, or $-O(R^4O)_q$ wherein R^4 is alkylene group having 1 to 4 carbon atoms, and q is an integer of 1 to 5,

R¹ is alkyl group having 1 to 24 carbon atoms, alkenyl group having 2 to 24 carbon atoms, or aryl group having 6 to 24 carbon atoms, each being optionally substituted by halogen atom partly or entirely,

R² is hydrogen atom, -OH, alkyl group, alkenyl group, or aryl group, each being optionally substituted by halogen atom partly or entirely.

[0021] Of the derivatives of aromatic polycarboxylic acid of Formula II, preferred are derivatives of phthalic acid, trimellitic acid, pyromellitic acid and anhydrides of the preceding acids. Specifically, preferred are monostearyl phthalate, monodecyl phthalate, monooctyl phthalamide, polyoxyethylenelauryl phthalate, monodecyl trimellitate, monostearyl trimellitate, monostearyl pyromellitate, and distearyl pyromellitate.

[0022] The conditions for mixing the derivative of aromatic polycarboxylic acid with the natural rubber latex may be selected depending on the kinds of natural rubber latex and the kinds of derivative of aromatic polycarboxylic acid to be used.

[0023] The amount of the added derivative of aromatic polycarboxylic acid is preferably 0.01 to 30% by weight based on the amount of the natural rubber latex. An added amount of less than 0.01% by weight may fail to sufficiently reduce a Mooney viscosity. An added amount exceeding 30% by weight creates no additional effect corresponding to the increased amount, and additionally, may adversely affect the reinforcing characteristic of vulcanized rubber. Although the added amount varies within the above range depending on the kind or grade of the natural rubber latex to be used, a range from 0.05 to 20% by weight is preferred in view of production costs and properties of the natural rubber master batch to be prepared.

[0024] In Step 1 for cleaving amide linkages of natural rubber latex, a surfactant is preferably used to enhance the stability of latex. The surfactant may be anionic, cationic, nonionic, and amphoteric, with anionic and nonionic surfactants being preferred. The amount of the added surfactant may be suitably selected depending on the properties of the natural rubber latex, and usually 0.01 to 2% by weight, preferably 0.02 to 1% by weight based on the natural rubber latex.

[0025] In Step 2 of the first method for producing the natural rubber master batch, is used a slurry prepared in advance by dispersing into water at least one filler selected from the group consisting of carbon black, silica and the inorganic fillers of Formula I. The method for preparing the slurry may be a known method, and not specifically limited.

[0026] The second method of the present invention for producing the natural rubber master batch includes a step for mixing a natural rubber latex with a slurry having been dispersed with at least one filler selected from the group consisting of carbon black, silica and an inorganic filler represented by the above Formula I, wherein it is required that (i) the particle size distribution of the filler in the aqueous slurry is 25 μm or less in terms of a volume average particle size (mv) and 30 μm or less in terms of a 90 volume % particle size (D90), and (ii) a 24M4DBP absorption of dried filler recovered from the slurry is 93% or more of that of a filler before dispersed into water.

[0027] The particle size distribution is preferably 20 μm or less by mv and 25 μm or less by D90. Excessively large particle size cause insufficient dispersion of filler in rubbers to decrease the reinforcing property and the abrasion resistance. In contrast, when a shearing force is excessively applied to the slurry to reduce the particle size, the aggregated structure of filler is broken to cause a lowering of the reinforcing property. Therefore, the 24M4DBP absorption of the dried filler recovered from the slurry is required to be maintained at 93% or more, preferably 96 or more, of that of the filler before made into the slurry.

[0028] In the first and second methods for producing the natural rubber master batch, the aqueous slurry of the filler is prepared by using a high-shear mixer of rotor-stator type, a high-pressure homogenizer, an ultrasonic homogenizer, a colloid mill, etc. For example, the slurry is prepared by charging predetermined amounts of a filler and water into a colloid mill, and then stirring the mixture for a certain period of time at high speed.

[0029] Carbon blacks generally used in rubber industries can be used in the present invention. For example, carbon blacks of various grades such as SAF, ISAF, HAF, FEF and GPF may be used alone or in combination.

[0030] Although silica used in the present invention is not specifically limited, precipitated silica, fumed silica and colloidal silica are preferably used.

[0031] The inorganic filler of Formula I may include alumina (Al_2O_3) such as γ -alumina and α -alumina; alumina monohydrate ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) such as böhmite and diasporite; aluminum hydroxide [$\text{Al}(\text{OH})_3$] such as gibbsite and bayerite; aluminum carbonate [$\text{Al}_2(\text{CO}_3)_2$]; magnesium hydroxide [$\text{Mg}(\text{OH})_2$]; magnesium oxide (MgO); magnesium carbonate (MgCO_3); talc ($3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$); attapulgite ($5\text{MgO} \cdot 8\text{SiO}_2 \cdot 9\text{H}_2\text{O}$); titanium white (TiO_2); titanium black (TiO_{2n-1}); calcium oxide (CaO); calcium hydroxide [$\text{Ca}(\text{OH})_2$]; aluminum magnesium oxide ($\text{MgO} \cdot \text{Al}_2\text{O}_3$); clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$); kaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$); pyrophyllite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$); bentonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot 2\text{H}_2\text{O}$); aluminum silicate (Al_2SiO_5 , $\text{Al}_4 \cdot 3\text{SiO}_4 \cdot 5\text{H}_2\text{O}$, etc.); magnesium silicate (Mg_2SiO_4 , MgSiO_3 , etc.); calcium silicate ($\text{Ca}_2 \cdot \text{SiO}_4$, etc.); aluminum calcium silicate ($\text{Al}_2\text{O}_3 \cdot \text{CaO} \cdot 2\text{SiO}_2$, etc.); magnesium calcium silicate (CaMgSiO_4); calcium carbonate (CaCO_3); zirconium oxide (ZrO_2); zirconium hydroxide [$\text{ZrO}(\text{OH})_2 \cdot n\text{H}_2\text{O}$]; zirconium carbonate [$\text{Zr}(\text{CO}_3)_2$]; and crystalline aluminosilicates having hydrogen, alkali metal or alkaline earth metal for compensating electric charges as in the case of various zeolites. Preferably, M¹ of Formula I is at least one member selected from the group consisting of aluminum metal, oxides or

hydroxides of aluminum, hydrates of oxides or hydroxides of aluminum, and carbonates of aluminum. The concentration of the filler selected from carbon black, silica and the inorganic fillers of Formula I in the slurry is preferably 0.5 to 60% by weight, more preferably 1 to 30% by weight based on the amount of the slurry.

[0032] The amount of the added filler selected from carbon black, silica and the inorganic fillers of Formula I is preferably 5 to 100 parts by weight, more preferably 10 to 70 parts by weight based on 100 parts by weight of the rubber component of the natural rubber master batch. When the filler is added in an amount less than 5 parts by weight, a sufficient reinforcing property cannot be obtained in some cases. An added amount exceeding 100 parts by weight is likely to deteriorate the processability. Carbon black, silica and the inorganic fillers of Formula I may be used singly or in combination of two or more.

[0033] The slurry and the natural rubber latex from the step for cleaving the amide linkages are mixed, for example, by adding the latex dropwise into the slurry in a homomixer under stirring, or vice versa, i.e., by adding the slurry dropwise into the latex under stirring. Alternatively, a flow of the slurry is mixed with a flow of the latex in a certain proportion under conditions for creating a vigorous hydraulic stirring.

[0034] The natural rubber master batch is coagulated, as employed in known methods, by using a coagulant, for example, acids such as formic acid and sulfuric acid and salts such as sodium chloride. In the present invention, the coagulation may proceed in some cases merely by mixing the natural rubber latex and the slurry without adding coagulant.

[0035] In addition to carbon black, silica and the inorganic filler of Formula I, the natural rubber master batch may be added, if desired, with various additives such as surfactants, vulcanizing agents, antioxidants, colorants and dispersants.

[0036] The final stage of the method for producing the natural rubber master batch is a drying step which may be carried out by using a usual dryer such as vacuum dryer, air dryer, drum dryer and band dryer. Preferably, the drying step is carried out by applying a mechanical shearing force to improve the dispersion of the filler. With such a drying operation, a rubber excellent in the processability, the reinforcing property and the low fuel consumption can be obtained. The drying under shearing force can be carried out by using a known kneader, preferably by a continuous kneader in view of industrial productivity. More preferably, a corotating or counterrotating twin-screw kneading extruder is used.

[0037] When the drying step is conducted under shearing force, the water content of the master batch before drying is preferably 10% or more. If the water content is less than 10%, the improvement in the dispersion of the filler is insufficient in the drying step.

[0038] The natural rubber master batch of the present invention is obtained by the methods described above. Alternatively, the natural rubber master batch is obtained by mixing a natural rubber latex having its amide linkages cleaved with a slurry having been prepared by dispersing into water at least one filler selected from the group consisting of carbon black, silica and the inorganic fillers of Formula I, and coagulating the mixture.

[0039] The natural rubber composition of the present invention is prepared by using the natural rubber master batch described above. Alternatively, the natural rubber composition is prepared by compounding natural rubber containing non-rubber components or the natural rubber master batch described above with silica and/or the inorganic filler of Formula I.

[0040] The natural rubber containing non-rubber components is obtained in the same manner as described above, namely, by a method of cleaving amide linkages in a natural rubber latex, particularly using protease or a derivative of aromatic polycarboxylic acid.

[0041] The average particle size of the silica and/or the inorganic filler to be used in the present invention is preferably 5 μm or less. When exceeding 5 μm , the reinforcing effect may become insufficient, the abrasion resistance may become poor, and the wet skid resistance may be deteriorated.

[0042] In addition to the silica and/or the inorganic filler, carbon black may be used as the filler. The carbon black is not particularly limited, and selected from known carbon blacks generally used as reinforcing filler.

[0043] The total amount of the added filler is 10 to 120 parts by weight based on 100 parts by weight of the rubber component. If less than 10 parts by weight, the desired reinforcing property and abrasion resistance cannot be attained. The amount exceeding 120 parts by weight is likely to cause the deterioration of the processability.

[0044] The natural rubber composition of the present invention may be further compounded with a coupling agent, if desired, to enhance the bonding between rubber molecules and the fillers. The coupling agent is not specifically limited, and those generally used in known rubber compositions may be used. Examples of the coupling agent include silane coupling agents such as bis(3-triethoxysilylpropyl) polysulfide, γ -mercaptopropyltriethoxysilane, γ -aminopropyltriethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, and N- β -aminoethyl- γ -aminopropyltrimethoxysilane; aluminum coupling agents; and titanate coupling agents. The addition amount of the coupling agent is selected from the range of 1 to 20 % by weight based on the filler.

[0045] The rubber composition of the present invention may be further compounded with various chemicals generally used in rubber industry, for example, vulcanizing agent, vulcanizing accelerator, antioxidant, scorch retarder, zinc oxide,

and stearic acid.

[0046] The present invention will be described in more detail with reference to the examples which should not be construed to limit the scope of the present invention thereto.

[0047] The measurements in the examples and comparative examples were made in the following manners.

(1) Particle size distribution of filler in aqueous slurry (volume average particle size (mv) and 90 volume % particle size (D90))

[0048] Measured by a laser diffraction particle size analyzer (Microtrac FRA Type) using a water solvent (refractive index: 1.33). In each measurement, the particle refractive index was regarded as 1.57. The measurements were conducted immediately after dispersion to prevent the filler from reaggregating together.

(2) 24M4DBP absorption

[0049] Measured according to ISO 6894.

(3) Mooney viscosity (ML_{1+4}) of rubber composition

[0050] Measure according to JIS K6300-1994 at 130°C. In Table 3, the results are expressed by indexed numbers while taken the result of Comparative Example 7 as 100 for Example 10 and Comparative Examples 7 and 8, and the result of Comparative Example 9 as 100 for Example 11 and Comparative Examples 9 and 10. The smaller the index number, the better the processability.

(4) Reinforcing property (tensile strength)

[0051] Tensile strength was measured at 23°C according to JIS K6251-1993. The larger the measured value, the higher the reinforcing property.

(5) Abrasion resistance

[0052] The abrasion wear was measured by a lambourn abrader machine at room temperature under a slip ratio of 40%. The reciprocal numbers of the measured abrasion wears were employed as the abrasion resistance. The results are expressed by indexed numbers while taken the result of Comparative Example 3 as 100 for Examples 1 to 5 and Comparative Examples 1 to 3, the result of Comparative Example 5 as 100 for Examples 6 to 8 and Comparative Examples 4 and 5, and the result of Comparative Example 6 as 100 for Example 9 and Comparative Example 6. The larger the indexed number, the better the abrasion resistance.

(6) Elastic modulus (M_{300})

[0053] The tensile stress at 300% elongation (M_{300}) was measured according to JIS K6251-1993. The results are expressed by indexed numbers while taken the result of Comparative Example 7 as 100 for Example 10 and Comparative Examples 7 and 8, and the result of Comparative Example 9 as 100 for Example 11 and Comparative Examples 9 and 10. The larger the value, the higher the elastic modulus.

(7) Aging property

[0054] The tensile strength was measured according to JIS K6257-1993 after heat aging at 100°C for 48 h in a Geer oven. The results are expressed by indexed numbers while taken the result of Comparative Example 7 as 100 for Example 10 and Comparative Examples 7 and 8, and the result of Comparative Example 9 as 100 for Example 11 and Comparative Examples 9 and 10. The larger the value, the better the aging property.

EXAMPLES 1-9 AND COMPARATIVE EXAMPLES 1-6

A. Preparation of latex

(i) Latex 1

[0055] A field latex of natural rubber (rubber content: 24.2%) was diluted with deionized water to a rubber content

of 20%.

(ii) Latex 2

5 [0056] Into Latex 1, were added 0.5% of an anionic surfactant (Demol N manufactured by Kao Corporation) and 0.1% of an alkaline protease (Alkalase 2.5L Type DX manufactured by Novozymes A/S). The mixture was stirred at 40°C for 8 h to cleave amide linkages in the natural rubber.

(iii) Latex 3

10 [0057] Like the preparation of Latex 2, 0.5% of an anionic surfactant (Demol N manufactured by Kao Corporation) and 3% of monostearyl phthalate were added to Latex 1. The mixture was stirred at 80°C for 12 h to cleave amide linkages in the natural rubber.

15 B. Preparation of aqueous slurry dispersed with filler

(i) Slurry 1

20 [0058] Into a colloid mill with a rotor diameter of 50 mm, 1425 g of deionized water and 75 g of carbon black (N110) were charged. The mixture was stirred for 10 min at a rotation speed of 1500 rpm under a rotor-stator gap of 1 mm.

(ii) Slurry 2

25 [0059] Prepared in the same manner as in the preparation of Slurry 1, except for stirring for 10 min at a rotation speed of 5000 rpm under a rotor-stator gap of 0.3 mm.

(iii) Slurry 3

30 [0060] To Slurry 1, 0.05% of an anionic surfactant (Demol N manufactured by Kao Corporation) was added. The mixture was circulated three times in a high pressure homogenizer under a pressure of 500 kPa.

(iv) Slurry 4

35 [0061] Prepared in the same manner as in the preparation of Slurry 3, except for circulated five times in the homogenizer under a pressure of 1000 kPa.

(v) Slurry 5

40 [0062] Into a colloid mill with a rotor diameter of 50 mm, 1425 g of deionized water and 75 g of precipitated silica (Nipsil LP manufactured by Nippon Silica Industrial Co., Ltd.) were charged. The mixture was stirred for 10 min at a rotation speed of 1500 rpm under a rotor-stator gap of 0.5 mm.

(vi) Slurry 6

45 [0063] Prepared in the same manner as in the preparation of Slurry 5, except for stirring for 10 min at a rotation speed of 7000 rpm under a rotor-stator gap of 0.3 mm.

(vii) Slurry 7

50 [0064] Into a colloid mill with a rotor diameter of 50 mm, 1425 g of deionized water and 75 g of gibbsite aluminum hydroxide (Higilite H-43M manufactured by Showa Denko K.K.) were charged. The mixture was stirred for 10 min at a rotation speed of 1500 rpm under a rotor-stator gap of 0.5 mm.

[0065] The particle size distribution (mv and D90) of the filler in each aqueous slurry prepared above and 24M4DBP absorption of the dried filler recovered from each aqueous slurry are shown in Table 1.

55

Table 1

	Slurry						
	1	2	3	4	5	6	7
Filler	CB	CB	CB	CB	silica	silica	Aluminum hydroxide
Particle size distribution (μm)							
mv	29.6	8.2	15.1	6.5	31.4	13.2	5.1
D90	38.3	12.4	19.5	11.1	44.6	24.0	8.8
Structure after recovery/drying							
24M4DBP (ml/100g)	97	95	96	88	145	144	52
Retention of 24M4DBP (%)	99.0	96.9	98.0	89.8	96.7	96.0	100.0

24M4DBP absorption of filler before made into slurry

Filler	24M4DBP (ml/100 g)
CB* ¹	98
Silica* ²	150
Aluminum hydroxide* ³	52

Note *¹Carbon black N110

*²Nipsil LP manufactured by Nippon Silica Industrial Co., Ltd.

*³Higilite H-43M manufactured by Showa Denko K.K.

C. Coagulation step

[0066] Into a homomixer, were charged each latex and slurry prepared above so that 50 parts by weight of the filler shown in Table 2 was mixed with 100 parts by weight of the rubber component. While stirring the mixture, formic acid was added until the mixture reached pH 4.5. The coagulated master batch was recovered, washed with water, and dehydrated until the water content was reduced to about 40%.

D. Drying step

[0067] The dehydrated master batch from the coagulation step was dried by (i) a band dryer method in which the drying was carried out at 120°C using a band dryer, or (ii) a twin-screw kneading extruder method in which the drying was carried out at a barrel temperature of 120°C under a rotation speed of 100 rpm using a twin-screw kneading extruder (corotating screw diameter: 30 mm; L/D = 35; three vent holes) manufactured by Kobe Steel, Ltd.

[0068] The content of filler in each master batch thus prepared was about 50 parts by weight based on 100 parts by weight of natural rubber.

[0069] In Comparative Examples 3, 5 and 6, 100 parts by weight of natural rubber (SMR), instead of a master batch, was mixed with 50 parts by weight of filler in a plastomill by a so-called dry kneading.

E. Preparation of rubber composition

[0070] Each filler-compounded rubber (100 parts by weight of natural rubber and 50 parts by weight of filler) prepared by master batch kneading or by dry kneading was compounded with 3 parts by weight of zinc oxide, 1.2 parts by weight of sulfur, 2 parts by weight of stearic acid, 1 part by weight of N-t-butyl-2-benzothiazolylsulfenamide (TBBS), 1 part by weight of N-phenyl-N'-1,3-dimethylbutyl-p-phenylenediamine (6C), and optionally 4 parts by weight of a silane coupling agent (Si69 (trademark) manufactured by Degussa Aktiengesellschaft) when silica was used as the filler. The mixture was kneaded in a plastomill to prepare each rubber composition.

[0071] The resulting rubber composition was tested for Mooney viscosity, and after vulcanization at 150°C for 30 min, tested for the tensile strength and abrasion resistance by the methods described above. The results are shown in Table 2.

Table 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Com. Ex. 1
Filler	CB	CB	CB	CB	CB
Compounding method	MB	MB	MB	MB	MB
Preparation of MB					
A latex	latex 1	latex 1	latex 1	latex 3	latex 1
B slurry	slurry 2	slurry 3	slurry 3	slurry 3	slurry 4
D drying	twin-screw extruder	band dryer	twin-screw extruder	twin-screw extruder	twin-screw extruder
Properties					
Mooney viscosity	77	85	80	74	75
Reinforcing property (tensile strength) (MPa)	30.6	29.3	30.5	30.2	24.9
Abrasion resistance (indexed number)	106	107	107	105	88

Table 2 (contd.)

	Com. Ex. 2	Ex. 5	Com. Ex. 3	Ex. 6	Ex. 7
Filler	CB	CB	CB	silica	silica
Compounding method	MB	MB	dry kneading	MB	MB
Preparation of MB					
A latex	latex 1	latex 2	—	latex 1	latex 1
B slurry	slurry 1	slurry 1	—	slurry 6	slurry 6
D drying	twin-screw extruder	twin-screw extruder	—	band dryer	twin-screw extruder
Properties					
Mooney viscosity	97	88	102	119	108
Reinforcing property (tensile strength) (MPa)	27.3	29.6	29.0	29.1	29.2
Abrasion resistance (indexed number)	97	102	100	104	104

Table 2 (contd.)

	Com. Ex. 4	Ex. 8	Com. Ex. 5	Ex. 9	Com. Ex. 6
5 Filler	silica	silica	silica	aluminum hydroxide	aluminum hydroxide
Compounding method	MB	MB	dry kneading	MB	dry kneading
Preparation of MB					
10 A latex	latex 1	latex 2	—	latex 1	—
B slurry	slurry 5	slurry 5	—	slurry 7	—
D drying	band dryer	band dryer	—	twin-screw extruder	—
Properties					
15 Mooney viscosity	131	120	132	55	66
Reinforcing property (tensile strength) (MPa)	24.6	27.8	26.7	23.5	21.4
Abrasion resistance (indexed number)	96	102	100	121	100

25 Note: CB is carbon black.

MB is master batch.

30 [0072] As shown in Table 2, Examples 1 to 5 and Comparative Examples 1 to 3 relates to compositions compounded with carbon black. The master batch was prepared by the second production method for Examples 1 to 3, by the first production method for Example 5, and by a method satisfying both the first and second production methods for Example 4. Upon comparing Examples 1 to 5 with Comparative Examples 1 and 2 in which the production methods of the present invention were not employed, it can be seen that the rubber compositions of Examples 1 to 5 are well balanced in the processability, reinforcing property and abrasion resistance at high level. The rubber composition of Comparative Example 3 which was prepared by dry kneading showed an extremely poor processability.

35 [0073] Examples 6 to 8 and Comparative Examples 4 and 5 relates to compositions compounded with silica. The master batch was prepared by the second production method for Examples 6 and 7, and by the first production method for Example 8. Upon comparing Examples 6 to 8 with Comparative Example 4 in which the production methods of the present invention were not employed, it can be seen that the rubber compositions of Examples 6 to 8 are well balanced in the processability, reinforcing property and abrasion resistance at high level. The rubber composition of Comparative Example 5 which was prepared by dry kneading showed an extremely poor processability.

40 [0074] Example 9 and Comparative Example 6 relates to compositions compounded with aluminum hydroxide. The master batch of Example 9 was prepared by the second production method of the present invention. Upon comparing Example 9 with Comparative Example 6 in which the dry kneading was employed, it can be seen that Example 9 is well balanced in the processability, reinforcing property and abrasion resistance at high level.

PREPARATION OF RUBBER COMPOSITION FOR TEST

50 PREPARATION EXAMPLE 1: Natural rubber I

(1) Step for cleaving amide linkages of natural rubber latex

55 [0075] Into a natural rubber latex containing 20% of rubber component, were added 0.5% of an anionic surfactant (Demi N manufactured by Kao Corporation) and 0.1% of an alkaline protease (Alkalase 2.5L Type DX manufactured by Novozymes A/S). The mixture was stirred at 40°C for 8 h.

(2) Step for coagulation and drying

[0076] The natural rubber latex from Step 1 was coagulated by acid to obtain a rubber product, which was then dried by passing five times through a drum dryer controlled at 130°C, and further dried in a vacuum dryer at 40°C for 8 h, thereby obtaining the natural rubber I.

PREPARATION EXAMPLE 2: Natural rubber II

[0077] The natural rubber latex (B) obtained in the amide-cleaving Step 1 of Preparation Example 1 was centrifuged at 10000 rpm for 30 min, and then, coagulated and dried in the same manner as in Preparation Example 1 to prepare the natural rubber II.

EXAMPLE 10

[0078] Each rubber composition was prepared by compounding 100 parts by weight of the natural rubber I prepared in Preparation Example 1, 40 parts by weight of silica and other compounding agents in respective amounts shown in Table 3. The rubber composition was tested for Mooney viscosity before vulcanization, and tested for elastic modulus (M_{300}) and aging property after vulcanization. The vulcanization was carried out at 150°C for 30 min. The results are shown in Table 3.

COMPARATIVE EXAMPLES 7 AND 8

[0079] Each rubber composition was prepared in the same manner as in Example 10, except for using, in place of the natural rubber I, a general natural rubber (SMR) or the natural rubber II prepared in Preparation Example 2. The results of evaluation tests are shown in Table 3.

EXAMPLE 11

[0080] A rubber composition was prepared in the same manner as in Example 10, except for using, in place of 40 parts by weight of silica, 30 parts by weight of silica and 30 parts by weight of aluminum hydroxide as the filler, and changing the amount of the silane coupling agent to 2 parts by weight. The results of evaluation tests are shown in Table 3.

COMPARATIVE EXAMPLES 9 AND 10

[0081] Each rubber composition was prepared in the same manner as in Example 11, except for using, in place of the natural rubber I, a general natural rubber (SMR) or the natural rubber II prepared in Preparation Example 2. The results of evaluation tests are shown in Table 3.

Table 3

	Com. Ex. 7	Com. Ex. 8	Ex. 10
5	Compounding Formulation		
	(part by weight)		
	Natural rubber		
	type or preparation method	SMR*1	Method 2
10	amount	100	Method 1
	Silica*2	40	100
	Aluminum hydroxide*3	—	40
	Silane coupling agent*4	3	—
15	Stearic acid	2	3
	Zinc oxide	2	2
	Vulcanization accelerator TBBS*5	3	3
	Sulfur	1.5	1.5
20	Mooney viscosity (ML ₁₊₄) at 130°C	100	81
	(indexed number)		85
	Elastic modulus (M ₃₀₀)	100	68
	(indexed number)		105
25	Aging property	100	86
	(indexed number)		110

Table 3 (contd.)

	Com. Ex. 9	Com. Ex. 10	Ex. 11
5 Compounding Formulation (part by weight)			
Natural rubber			
type or preparation method	SMR* ¹	Method 2	Method 1
10 amount	100	100	100
Silica* ²	30	30	30
Aluminum hydroxide* ³	20	20	20
Silane coupling agent* ⁴	2	2	2
Stearic acid	2	2	2
15 Zinc oxide	3	3	3
Vulcanization accelerator TBBS* ⁵	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5
Mooney viscosity (ML ₁₊₄) at 130°C	100	86	87
20 (indexed number)			
Elastic modulus (M ₃₀₀)	100	62	107
(indexed number)			
Aging property	100	90	104
25 (indexed number)			
Note			
* ¹ SMR: Natural rubber (Standard Malaysian Rubber)			
* ² Silica: Nipsil AQ (trademark) manufactured by Nippon Silica Industrial Co.,			
30 Ltd.			
* ³ Aluminum hydroxide: Higilite H-43 (trademark) manufactured by Showa			
35 Denko K.K.			
* ⁴ Silane coupling agent: Si69 (trademark) manufactured by Degussa			
Aktiengesellschaft			
40 * ⁵ Vulcanization accelerator TBBS: N-t-butyl-2-benzothiazolylsulfenamide			

[0082] The rubber compositions of inventive Examples 10 and 11 were prepared by using the natural rubber I which had been prepared from the natural rubber latex with its amide linkages cleaved and which had non-rubber components. As seen from the above Table, the rubber compositions of Examples 10 and 11, as compared with Comparative Examples 7 and 9, are excellent in the processability because of their low Mooney viscosities and are improved in the elastic modulus and the aging property. The rubber compositions of Comparative Examples 8 and 10 are extremely poor in the elastic modulus and the aging property because the rubber compositions were prepared from the natural rubber II from which the non-rubber component was removed by centrifugation after cleaving amide linkages.

[0083] As described above, according to the production method of the natural rubber latex of the present invention, a natural rubber composition improved in the processability, the reinforcing property, and the abrasion resistance can be obtained. The natural rubber composition of the present invention is largely improved in its processability without adversely affecting the elastic modulus and the aging property inherent to natural rubber. A tire produced by using the rubber composition is well blanching in all the properties such as wet skid resistance, low fuel consumption and abrasion resistance at high level. Therefore, the present invention is applicable to tire applications as well as belts, hoses, rubber vibration insulators, and other rubber products.

Claims

1. A method for producing a natural rubber master batch, which comprises a step for cleaving amide linkages in a natural rubber latex; and a step for mixing the latex having its amide linkages cleaved with an aqueous slurry having been dispersed with at least one filler selected from the group consisting of carbon black, silica and an inorganic filler represented by the following Formula I:



wherein M^1 is at least one member selected from the group consisting of metals of aluminum, magnesium, titanium, calcium and zirconium, oxides of the preceding metals, hydroxides of the preceding metals, hydrates of the preceding oxides and hydroxides, and carbonates of the preceding metals; n is an integer of 1 to 5; x is an integer of 0 to 10; y is an integer of 2 to 5; and z is an integer of 0 to 10.

2. A method for producing a natural rubber master batch, which comprises a step for mixing a natural rubber latex with an aqueous slurry having been dispersed with at least one filler selected from the group consisting of carbon black, silica and an inorganic filler represented by Formula I as defined in Claim 1, wherein (i) the particle size distribution of the filler in the aqueous slurry is 25 μm or less in terms of a volume average particle size (mv) and 30 μm or less in terms of a 90 volume % particle size (D90), and (ii) a 24M4DBP absorption of dried filler recovered from the aqueous slurry is maintained at 93% or more of that of the filler before dispersed into water.
3. The method according to Claim 2, wherein the natural rubber latex is subjected to a step for cleaving amide linkages in the latex.
4. The method according to Claim 1 or 3, wherein a protease and/or a derivative of aromatic polycarboxylic acid is used in the step for cleaving amide linkages.
5. The method according to Claim 4, wherein the protease is an alkaline protease.
6. The method according to any one of Claims 1 to 5, wherein a surfactant is added to the natural rubber latex and/or the aqueous slurry.
7. The method according to any one of Claims 1 to 6, wherein the silica is precipitated silica, fumed silica or colloidal silica.
8. The method according to any one of Claims 1 to 6, wherein the inorganic filler of Formula I is at least one member selected from the group consisting of alumina (Al_2O_3); alumina monohydrate ($Al_2O_3 \cdot H_2O$); aluminum hydroxide [$Al(OH)_3$]; aluminum carbonate [$Al_2(CO_3)_2$]; magnesium hydroxide [$Mg(OH)_2$]; magnesium oxide (MgO); magnesium carbonate ($MgCO_3$); talc ($3MgO \cdot 4SiO_2 \cdot H_2O$); attapulgite ($5MgO \cdot 8SiO_2 \cdot 9H_2O$); titanium white (TiO_2); titanium black (TiO_{2n-1}); calcium oxide (CaO); calcium hydroxide [$Ca(OH)_2$]; aluminum magnesium oxide ($MgO \cdot Al_2O_3$); clay ($Al_2O_3 \cdot 2SiO_2$); kaolin ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$); pyrophyllite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$); bentonite ($Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$); aluminum silicate (Al_2SiO_5 , $Al_4 \cdot 3SiO_4 \cdot 5H_2O$); magnesium silicate (Mg_2SiO_4 , $MgSiO_3$); calcium silicate ($Ca_2 \cdot SiO_4$, etc.); aluminum calcium silicate ($Al_2O_3 \cdot CaO \cdot 2SiO_2$); magnesium calcium silicate ($CaMgSiO_4$); calcium carbonate ($CaCO_3$); zirconium oxide (ZrO_2); zirconium hydroxide [$ZrO(OH)_2 \cdot nH_2O$]; zirconium carbonate [$Zr(CO_3)_2$]; and crystalline aluminosilicates.
9. The method according to any one of Claims 1 to 6, wherein M^1 of Formula I is at least one member selected from the group consisting of aluminum metal, oxides of aluminum, hydroxides of aluminum, hydrates of the oxides and hydroxides and carbonates of aluminum.
10. The method according to any one of Claims 1 to 9, further comprising a step for drying a coagulated natural rubber master batch while applying a mechanical shearing force.
11. The method according to Claim 10, wherein the drying step is carried out in a continuous kneader.
12. The method according to Claim 11, wherein the continuous kneader is a twin-screw kneading extruder.

13. A natural rubber master batch produced by:

a step for mixing a natural rubber latex having its amide linkages cleaved and an aqueous slurry having been dispersed with at least one filler selected from the group consisting of carbon black, silica and an inorganic filler represented by the following Formula I:



wherein M^1 is at least one member selected from the group consisting of metals of aluminum, magnesium, titanium, calcium and zirconium, oxides of the preceding metals, hydroxides of the preceding metals, hydrates of the preceding oxides and hydroxides, and carbonates of the preceding metals; n is an integer of 1 to 5; x is an integer of 0 to 10; y is an integer of 2 to 5; and z is an integer of 0 to 10; and a step for coagulating the resulting mixture.

14. A natural rubber master batch produced by the method as described in Claim 2.

15. A natural rubber master batch produced by the method as described in Claim 3.

16. A rubber composition comprising the natural rubber master batch as described in any one of Claims 13 to 15.

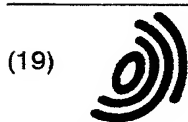
17. A natural rubber composition comprising (A) a natural rubber containing a non-rubber component which is obtained by cleaving amide linkages of a natural rubber latex and (B) silica and/or an inorganic filler represented by the following Formula I:



wherein M^1 is at least one member selected from the group consisting of metals of aluminum, magnesium, titanium, calcium and zirconium, oxides of the preceding metals, hydroxides of the preceding metals, hydrates of the preceding oxides and hydroxides, and carbonates of the preceding metals; n is an integer of 1 to 5; x is an integer of 0 to 10; y is an integer of 2 to 5; and z is an integer of 0 to 10.

18. The natural rubber composition according to Claim 17, further comprises a coupling agent.

19. A tire produced by using the rubber composition as described in any one of Claims 16 to 18.



(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 283 219 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
20.08.2003 Bulletin 2003/34

(51) Int Cl.7: **C08C 1/04**, C08J 3/22,
C08J 3/215
// C08L7:02

(43) Date of publication A2:
12.02.2003 Bulletin 2003/07

(21) Application number: **02255103.0**

(22) Date of filing: **22.07.2002**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
IE IT LI LU MC NL PT SE SK TR**
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **27.07.2001 JP 2001227748**
27.07.2001 JP 2001228123

(71) Applicant: **BRIDGESTONE CORPORATION**
Tokyo 104-0031 (JP)

(72) Inventors:
• Yanagisawa, Kazuhiro,
Bridgestone Cor. Tech. Cen.
Kodaira-shi, Tokyo 187-0031 (JP)
• Someno, Kazuaki, Bridgestone Cor. Tech. Center
Kodaira-shi, Tokyo (JP)
• Mukai, Uchu, Bridgestone Cor. Tech. Center
Kodaira-shi, Tokyo (JP)

(74) Representative: **Lamb, Martin John Carstairs
MARKS & CLERK,**
57-60 Lincoln's Inn Fields
London WC2A 3LS (GB)

(54) **Natural rubber master batch, production method thereof, and natural rubber composition**

(57) The natural rubber master batch of the present invention is prepared by mixing a natural rubber latex having its amide linkages cleaved and an aqueous slurry having a filler dispersed in water. Alternatively, the natural rubber master batch is prepared by a method including a step for mixing a natural rubber latex and an aqueous slurry containing dispersed fillers having a spe-

cific particle size distribution and a limited range of 24M4DBP absorption. The natural rubber composition of the present invention is prepared by compounding natural rubber, which contains non-rubber components prepared by cleaving amide linkages of natural rubber latex, with silica and/or a particular inorganic filler.

EP 1 283 219 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 02 25 5103

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InCL.7)
Y	US 4 029 633 A (HAGOPIAN ERIVAN ET AL) 14 June 1977 (1977-06-14) * claims 1,2 * * column 3, line 1 - line 7 *	1-7,10, 13-19	C08C1/04 C08J3/22 C08J3/215 //C08L7:02
D,Y	EP 0 584 597 A (SUMITOMO RUBBER IND ;KAO CORP (JP)) 2 March 1994 (1994-03-02) * claims 1,4,5,16,17 * * page 9, line 18 - line 27 *	1-7,10, 13-19	
D,A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 08, 30 June 1999 (1999-06-30) & JP 11 071408 A (SUMITOMO RUBBER IND LTD), 16 March 1999 (1999-03-16) * abstract *	1	
A	US 5 908 893 A (KAWASAKI ATSUKO ET AL) 1 June 1999 (1999-06-01) * claims 1-3,5 *	1	
A	DATABASE WPI Section Ch, Week 197629 Derwent Publications Ltd., London, GB; Class A12, AN 1976-55265X XP002245219 & JP 51 065150 A (MITSUBISHI CHEM IND LTD), 5 June 1976 (1976-06-05) * abstract *	1	TECHNICAL FIELDS SEARCHED (InCL.7) C08J C08C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 June 2003	Examiner Niaounakis, M
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03/02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 25 5103

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-06-2003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4029633	A	14-06-1977	AU 505709 B2	29-11-1979
			AU 2391277 A	12-10-1978
			BE 853516 A1	01-08-1977
			BR 7702088 A	24-01-1978
			CA 1057440 A1	26-06-1979
			CS 191339 B2	29-06-1979
			DE 2714265 A1	03-11-1977
			ES 457790 A1	01-03-1978
			FR 2348240 A1	10-11-1977
			GB 1567855 A	21-05-1980
			HK 92884 A	30-11-1984
			IN 144760 A1	01-07-1978
			IT 1082497 B	21-05-1985
			JP 52151338 A	15-12-1977
			JP 54010576 B	08-05-1979
			MY 36584 A	31-12-1984
			NL 7703608 A	18-10-1977
			PL 105366 B1	31-10-1979
			SG 56383 G	27-07-1984
			SU 910124 A3	28-02-1982
EP 0584597	A	02-03-1994	JP 2905005 B2	14-06-1999
			JP 6056902 A	01-03-1994
			JP 3115422 B2	04-12-2000
			JP 6056903 A	01-03-1994
			JP 2938282 B2	23-08-1999
			JP 6056904 A	01-03-1994
			JP 2977673 B2	15-11-1999
			JP 6056905 A	01-03-1994
			JP 3150434 B2	26-03-2001
			JP 6056906 A	01-03-1994
			AU 4445693 A	10-02-1994
			CN 1295082 A	16-05-2001
			CN 1086520 A ,B	11-05-1994
			DE 69318492 D1	18-06-1998
			DE 69318492 T2	08-10-1998
			EP 0584597 A1	02-03-1994
			EP 0805163 A2	05-11-1997
			ES 2116374 T3	16-07-1998
			KR 269837 B1	16-10-2000
			US 6239253 B1	29-05-2001
			US 6204358 B1	20-03-2001
			US 6335407 B1	01-01-2002
JP 11071408	A	16-03-1999	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 02 25 5103

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-06-2003

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5908893	A	01-06-1999	JP	8143606 A	04-06-1996
			US	6306955 B1	23-10-2001
JP 51065150	A	05-06-1976	JP	1086211 C	26-02-1982
			JP	56014694 B	06-04-1981

EPO FORM P0489

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82